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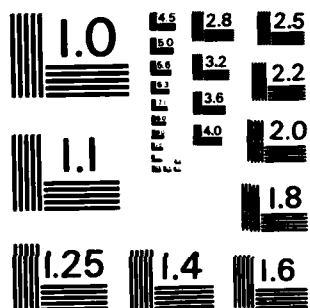
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TECHNICAL REPORT No. 29

ELECTROGENERATED CHEMILUMINESCENCE. 42.

The Electrochemistry and Electrogenerated Chemiluminescence of
the Tris(2,2'-bipyrazine)ruthenium(II) System.

by

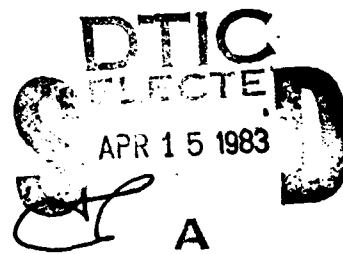
Jaime Gonzales-Velasco,* Israel Rubinstein,* R. J. Crutchley,#

A. B. P. Lever,# and Allen J. Bard*

#Department of Chemistry
York University
Downsview, Ontario
Canada M3J 1P3

*The University of Texas at Austin
Department of Chemistry
Austin, Texas 78712

March 31, 1983



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ELECTROGENERATED CHEMILUMINESCENCE. 42.

The Electrochemistry and Electrogenerated Chemiluminescence of
the Tris(2,2'-bipyrazine)ruthenium(II) System.

Jaime Gonzales-Velasco,^{1a,c} Israel Rubinstein,^{1a} R. J. Crutchley,^{1b}
A. B. P. Lever,^{1b} and Allen J. Bard*^{1a}

Department of Chemistry
The University of Texas
Austin, TX 78712

Department of Chemistry
York University
Downsview, Ontario
Canada M3J 1P3

Abstract

The electrochemical behavior and electrogenerated chemiluminescence (ecl) of $\text{Ru}(\text{bpz})_3^{2+}$ (as the PF_6^- salt) in acetonitrile solutions was investigated. Oxidation to the +3 form and reduction to the +1, 0, -1 and -2 forms occur at potentials about 0.5V more positive than the corresponding bipyridine complex. Emission characteristic of $\text{Ru}(\text{bpz})_3^{2+}$ is produced upon the electron transfer reaction between the +3 and +1 species. Weak emission also results from reaction of the +3 species with solvent or impurities.

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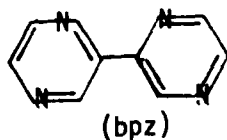
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Introduction.

Of the numerous compounds that produce chemiluminescence upon the electron transfer reactions of electrogenerated species (ecl), that observed with the $\text{Ru}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridine) system is among the most intense and best characterized.²⁻⁴ A recent report⁵ of a new, related compound, $\text{Ru}(\text{bpz})_3^{2+}$ (bpz = 2,2'-bipyrazine) and its spectroscopic and photocatalytic properties suggested a study of the electrochemical and ecl behavior of this compound.



Previous studies of $\text{Ru}(\text{bpy})_3^{2+}$ showed that ecl is produced by the redox reaction between the +1 and +3 species as well as by reaction of the +3 species with a number of reductants (e.g., especially oxalate).^{2d} We were particularly interested in $\text{Ru}(\text{bpz})_3^{2+}$ because the redox processes are shifted by $\sim 0.5\text{V}$ towards more positive potentials, compared with $\text{Ru}(\text{bpy})_3^{2+}$. This could prove valuable in ecl in aqueous media where proton reduction interferes at negative potentials. A comparison of the ecl efficiency between the bpz and bpy complexes is also of interest.

In this paper we describe the electrochemical behavior of the $\text{Ru}(\text{bpz})_3^{2+}$ system in acetonitrile (MeCN) solutions and demonstrate the production of ecl and its characteristics.

Experimental.

Chemicals. The $\text{Ru}(\text{bpz})_3^{2+}$ was obtained in the form of PF_6^- salt.⁵ It was recrystallized from MeCN and dried for 25 hr under vacuum at room temperature. The tetra-n-butylammonium hexafluorophosphate (TBAFP) used as supporting electrolyte was prepared by reaction of NH_4PF_6 (Ozark-Mahoning) and tetra-n-butylammonium perchlorate (Aldrich). The precipitate of TBAFP obtained was filtered and repeatedly washed with distilled water. The precipitate was dissolved in boiling EtOH; upon cooling, TBAFP was obtained in the form of small crystals. This procedure was repeated three times. Finally the crystals were recrystallized from a mixture of acetone and ether and dried under a vacuum.

Spectroquality grade acetonitrile (MCB) was degassed by freeze-pump-thaw cycles ($< 10^{-5}$ torr). A MeCN/0.1 M TBAFP solution did not show appreciable faradaic currents at a Pt electrode between -2.6 and +2.5 V vs the Ag wire quasireference electrode (AgRE).

Apparatus. A Princeton Applied Research (PAR) Model 173 Potentiostat and a PAR Model 175 Universal Programmer were used for voltammetric experiments. The output of the PAR Model 176 current follower was recorded directly using a Houston Instruments Model 2000 x-y recorder. The coulometric experiments employed a PAR 179 digital coulometer.

Procedure. The test solutions were prepared under He in a Vacuum Atmospheres Glove Box equipped with a Model MO 40-1 Dri-Train. Electrochemical and ecl experiments were carried out in a three compartment working cell with a volume of 3 cm^3 . The working electrode compartment was provided with an optically flat Pyrex glass window of approximately 2 cm^2 and the working electrode, a polished platinum disk, area = 0.06 cm^2 , was

aligned parallel to the window. The distance between the working electrode and the window was around 3 mm. The counterelectrode was a platinum foil, area = 3 cm². A silver wire immersed in the MeCN/TBAFP solution and separated from the working electrode chamber by a medium porosity frit was used as a quasireference electrode (AgRE). The potential of this Ag wire electrode was measured against an aqueous saturated calomel electrode (SCE) and checked vs the ferrocene/ferrocenium couple in MeCN and was found to have a potential of +0.055 V vs SCE.

The ecl measurements were carried out after transferring the sealed working cell to a light-tight box whose interior was painted with black nonreflective paint. The emitted light was measured with a Hamamatsu TV Corp. R928 photomultiplier tube. The ecl spectrum was taken by using an Oriel Co. monochromator. Emission and absorption spectra were obtained with an Aminco-Bowman spectrophotofluorometer (SPF) without slits for ecl studies and a Cary Model 14 UV and visible spectrophotometer, respectively.

Results and Discussion.

Electrochemical results. A typical cyclic voltammogram (CV) for 1 mM Ru(bpz)₃²⁺ in MeCN, 0.1 M TBAFP is shown in Figure 1. The peak potentials for the oxidation (E_{pa}) and reduction (E_{pc}) waves and ΔE_p values for each wave are given in Table 1. The general electrochemical behavior of the Ru(bpz)₃²⁺ system is very similar to that of Ru(bpy)₃²⁺ in MeCN, but there are significant differences. The reductions to the +1, 0, and -1 species and the oxidation to the +3 species occur with all peaks shifted 0.5 V towards more positive potentials as compared to the bpy complex. Thus the Ru(bpz)₃³⁺ species is a significantly stronger oxidant than is Ru(bpy)₃³⁺, and its production from the +2 form occurs much nearer to the anodic limit of the MeCN,TBAFP solution. Because of this, the Ru(bpz)₃³⁺ is less stable

than the bpy complex in this medium, which leads to differences in the characteristics of the +3/+2 wave and the ecl. On the other hand the fourth reduction wave (marked V in Figure 1) shows a well-defined reversal peak at a scan rate, v , of 100 mV/s at room temperature, indicating some stability of the -2 species. No such stability is observed with the corresponding bpy form that is produced at a potential about 0.5 V more negative. Only at $v > 20$ V/s or at temperatures of -30°C was any reversal anodic peak seen for the corresponding bpy wave.² However, repeated scanning over wave V to produce the reduced -2 form led to the formation of a deep brown solution caused by decomposition of this species. Moreover the rest potential of this solution after this cycling was -0.2 V vs AgRE as compared to the initial value of about +0.54 V, indicating irreversible production of a reduced species. The resulting brown solution could not be electrochemically oxidized back to the original orange $\text{Ru}(\text{bpz})_3^{2+}$ solution. Similar, but slower decomposition occurred upon scanning or holding the potential at values corresponding to peaks III and IV (Figure 1).

The one electron nature of the waves was confirmed by controlled potential coulometry (CPC) measurements. Reduction at -0.8 V vs AgRE near the peak of the first reduction wave (wave II, Figure 1) gave n_{app} (corresponding to number of Faradays per mole) of 0.98. Oxidation of the reduced solution back to the +2 form showed $Q_b/Q_f \approx 0.9$ (where Q_f and Q_b are the number of coulombs consumed during the forward reduction and reverse oxidation, respectively)^{6a} for an experimental duration of ~ 1 hr. This demonstrates the relatively high stability of the +1 species.

Cyclic voltammetric data for the reduction waves (II, III and IV) shown in Figure 1 are contained in Table 2. Because of the close spacing of the reduction waves it was difficult to determine precise values for peak

currents (i_{pc} and i_{pa}) and potentials. However, the current functions ($i_{pc}/v^{1/2}$) for all three waves are about the same, demonstrating that all three are one-electron transfers. Moreover, the values of $i_{pa}/i_{pc} \approx 1$ for these waves demonstrate that the +1, 0 and -1 forms are stable on the CV time scale.

For wave II the value of i_{pa}/i_{pc} is significantly larger than 1; this suggests that some deposition or adsorption of the +1 species occurs on the electrode. Although the CV data shows stability of the 0 and -1 forms on the short time scale, repeated cycling through these waves causes some color change in the solution as well as the formation of a deposit on the electrode surface.

As for wave I, corresponding to the +3/+2 oxidation-reduction process, the potential for this wave is close to the anodic stability limit of Pt in MeCN and the $\text{Ru}(\text{bpz})_3^{3+}$ species reacts with a component in the MeCN, TBAFP medium to regenerate the +2 species, giving rise to a catalytic wave.^{6b} The CV parameters for wave I confirm the catalytic nature of this wave. For example, as shown in Figure 2, the ratio of peak heights i_{pa}/i_{pc} , or peak areas Q_a/Q_c increases sharply with decreasing v . At low scan rates, the ratio Q_a/Q_c is very high since the +2 species is continuously regenerated during the scan. At higher scan rates the ratio approaches unity because no appreciable reaction of the +3 form occurs at short times.

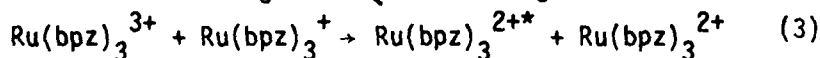
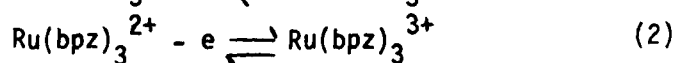
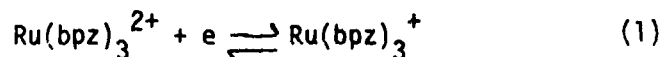
A voltammogram taken after repeated application of pulses between -0.8 and +1.9 V vs AgRE (the range for e1, as described below), as shown in Figure 3, suggests decomposition of the $\text{Ru}(\text{bpz})_3^{2+}$ complex since new peaks at +1.5 V vs AgRE near wave I and at -0.4 V vs. AgRE before Wave II appear. The new anodic peak at +1.5 V appears after a cathodic scan to -1.2 V and the new cathodic one at -0.4 V appears after a scan to +2.2 V. The species

giving rise to these waves is not known.

After these repeated pulsing experiments, the electrode surface was covered with a yellowish-brown precipitate. Although the nature of this precipitate was not elucidated, it probably can be attributed to the formation of reduced Ru-species. The decomposition process is enhanced when the cathodic scan limit is more negative.

Emission spectrum of $\text{Ru}(\text{bpz})_3^{2+}$. The emission spectrum of a 10^{-5} M solution of $\text{Ru}(\text{bpz})_3^{2+}$ in MeCN at room temperature is shown in Figure 4. An excitation wavelength for maximum absorption (435 nm) leads to the emission maximum at 585 nm for the luminescence of the sample. This wavelength is 25 nm shorter than the emission maximum of $\text{Ru}(\text{bpy})_3^{2+}$.

Ecl spectrum of $\text{Ru}(\text{bpz})_3^{2+}$ in acetonitrile. By pulsing the potential applied to the platinum electrode between 1.95 V and -0.85 V vs AgRE an orange ecl emission was observed. The light intensity obtained was lower than that for $\text{Ru}(\text{bpy})_3^{2+}$ under equivalent conditions, and decayed more rapidly. The ecl spectrum of the $\text{Ru}(\text{bpz})_3^{2+}$ (Figure 5) shows an emission maximum at 585 nm, identical to the emission spectrum obtained on photoexcitation. These results are similar to those obtained with $\text{Ru}(\text{bpy})_3^{2+}$. The mechanism for emission is probably the same in both cases, namely, reaction of the +3 and +1 forms to yield the +2 excited state:



This homogeneous redox reaction has a free energy of -2.7 eV (as calculated from the E_p values of the +3/+2 and +2/+1 waves and assuming an entropic contribution of 0.1 eV).⁷ This is greater than the energy of the emitting charge transfer state, 2.12 eV. The singlet excited state for the

$\text{Ru}(\text{bpz})_3^{2+}$ occurs at 2.85 eV^8 so that direct population of this state does not appear possible, and direct formation of the emitting triplet is proposed. This is analogous to the results in the $\text{Ru}(\text{bpy})_3^{2+}$ system.²⁻⁴

Characteristics of the ecl. Recent studies^{2e,3} of the ecl intensity $(t_r/t_f)^{-1/2}$ behavior (where t_f is forward pulse time and t_r the reverse pulse time) for the $\text{Ru}(\text{bpy})_3^{2+}$ system at short times $[(t_r/t_f)^{-1/2}$ of 1 to 10] showed that these Feldberg-Faulkner plots^{9,10} corresponded closely to that expected of an "S-route" system, where direct population of the emitting state on electron transfer occurs. Similar plots for the $\text{Ru}(\text{bpz})_3^{2+}$ system are shown in Figure 6. When either the +1 (Figure 6a) or +3 (Figure 6b) form is generated first, the behavior is very different from that of the theoretical model, which predicts a slope of -1.42. The cause for this deviation is probably the instability of the +3 form and perhaps quenching by decomposition products. This non-ideal behavior is also apparent from the ecl intensity-time transient itself (Figure 7). The anodic transient (following production of the +1 species) shows a peak which decays to an almost steady value. This attainment of a steady value is also apparent from the change in slope in the plot of Figure 6a. The following cathodic transient is very sharp and decays rapidly to background. The steady level of emission during the anodic pulse represents a reaction of the +3 species with solvent, electrolyte, or impurities to produce emission. That this is clearly the case can be seen from the anodic transient in Figure 8, where the potential was maintained at +1.90 V and a constant weak emission was observed. Recent studies have shown that the reaction of $\text{Ru}(\text{bpy})_3^{3+}$ with oxalate, organic acids or other reductants results in emission,^{2d,11,12} so a similar reaction by the stronger oxidant $\text{Ru}(\text{bpz})_3^{3+}$ appears reasonable. Thus the anodic step involves the +1/+3 electron

transfer reaction as well as the +3/background emission. During the subsequent cathodic step the +3 species has been depleted by this background reaction and less is available to react with the generated +1 species, producing the rapid decay of intensity.

Conclusions.

The electrochemical behavior of the $\text{Ru}(\text{bpz})_3^{2+}$ system generally parallels that of the corresponding bpy system, but shifted by about 0.5 V towards more positive potentials. Since the +2/+3 wave is best represented by electron transfers involving metal centers, the shift must be ascribed to greater stabilization of the +2 vs the +3 form by the bpz. The reduction waves, e.g., the +2/+1, are better represented as reduction of the ligands and the shift here represents easier reduction of bpz to the Ru^{2+} stabilized bpz^- species compared to bpy. The positive potential shift results in the +2/bpz species being less stable in MeCN than the corresponding bpy species. Ecl reactions involving the +3/+1 electron transfer annihilation reaction and a reaction of +3 with solvent or impurity to produce the $\text{Ru}(\text{bpz})_3^{2+}$ excited states occur. There is precedence for both of these in the bpy system.

Acknowledgement.

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Notes and References.

1. (a) University of Texas; (b) York University; (c) permanent address: Faculty de Ciencias, Universite Autonoma de Madrid, Ciudad Universite de Canto Blanco, Madrid 34, Spain.
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Figure Captions.

- Figure 1: Cyclic voltammogram of 1 mM $\text{Ru}(\text{bpz})_3^{2+}(\text{PF}_6^-)_2/\text{MeCN}/0.1 \text{ M}$ TBAFP at a Pt electrode. Scan rate, 100 mV/s^{-1} . $T = 25^\circ \text{ C}$. Reference electrode, Ag wire.
- Figure 2: Ratio between the anodic and cathodic charges in wave I as a function of the scan rate. $T = 25^\circ \text{ C}$. Solution same as Figure 1.
- Figure 3: Cyclic voltammogram of 1 mM $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2/\text{MeCN}/0.1 \text{ M}$ TBAFP after repeated pulsing between -0.8 and $+1.9 \text{ V}$ vs AgRE.
- Figure 4: Luminescence spectrum of a 10^{-5} M solution of $\text{Ru}(\text{bpz})_3^{2+}$ in MeCN at room temperature.
- Figure 5: ECL spectrum of a 1 mM $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2/\text{MeCN}/0.1 \text{ M}$ TBAFP solution. Pulsing limits: -0.8 V and $+1.85 \text{ V}$ vs AgRE. at 0.5 Hz .
- Figure 6: Feldberg-Faulkner plots for the solution in Figure 1. (a) precursor, $\text{Ru}(\text{bpz})_3^+$; (b) precursor, $\text{Ru}(\text{bpz})_3^{3+}$.
- Figure 7: Typical ecl intensity-time transient (I_{ecl} in arbitrary units). $T = 25^\circ \text{ C}$. Same solution as Figure 1.
- Figure 8: Ecl intensity-time transient obtained by pulsing between -0.85 V and $+1.9 \text{ V}$ vs AgRE for 3 sec and holding the potential at $+1.9 \text{ V}$. Same solution as in Figure 1.

TABLE 1

Cyclic Voltammetric Peak Potentials (E_p) for $\text{Ru}(\text{bpz})_3^{2+}$ in
0.1 M TBAPF-acetonitrile Solutions at a Platinum Electrode, $T = 25^\circ \text{C}$. ^a

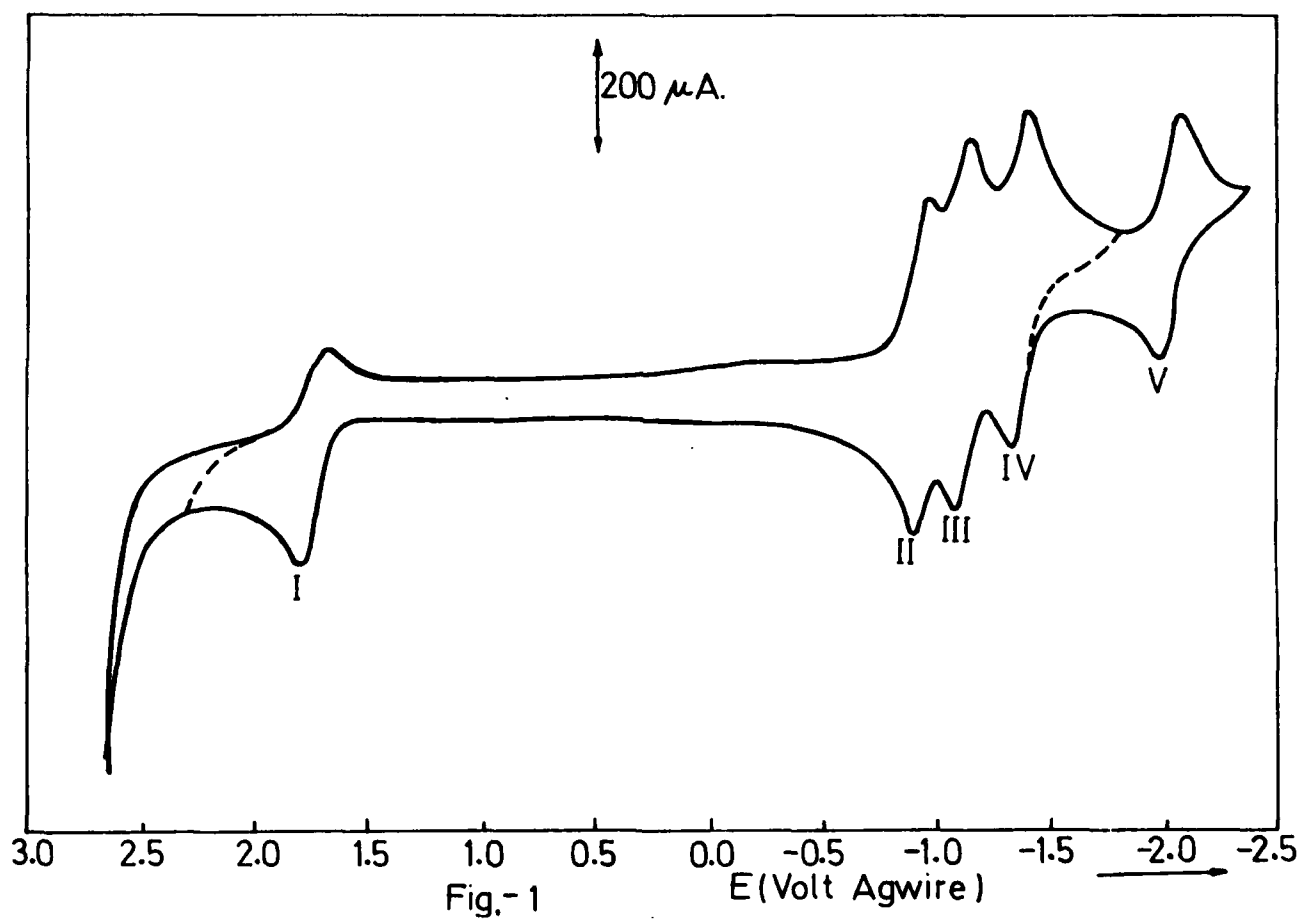
	<u>Peaks in Fig. 1</u>				
	I	II	III	IV	V
E_{pc} (reduction) (V vs Agre)	+1.85	-0.800	-0.980	-1.250	-2.075
E_{pa} (oxidation)	+1.94	-0.730	-0.910	-1.180	-1.975
Number of electrons	1	1	1	1	1
ΔE_p (25°C , 100 mV/s)	90	70	70	70	100
Redox states	3+/2+	2+/1+	1+/0	0/-1	-1/-2

^a Potential values were measured against an Ag wire quasireference electrode in the same solution. The Ag wire showed a potential of +55 mV measured against a SCE in the same solution.

Table 2
Cyclic Voltammetric Results for the Three Reductions of $\text{Ru}(\text{bpz})_3^{2+}$ ^a

Peak II				Peak III			Peak IV		
v (mV/s)	ΔE_p (mV)	$\frac{i_{pa}}{i_{pc}}$	$\frac{i_{pc}}{v^{1/2}C}$	ΔE_p (mV)	$\frac{i_{pa}}{i_{pc}}$	$\frac{i_{pc}}{v^{1/2}C}$	ΔE_p (mV)	$\frac{i_{pa}}{i_{pc}}$	$\frac{i_{pc}}{v^{1/2}C}$
10	30	1.00	1.2	60	1.00	1.4	70	0.88	1.2
20	60	1.40	1.0	60	0.97	1.6	60	0.88	1.3
50	60	1.00	1.0	60	1.28	1.2	70	0.90	1.4
100	60	1.11	0.9	80	1.00	1.7	70	0.83	1.7
200	70	1.45	0.6	80	1.03	1.2	90	0.75	1.6
500	90	1.28	0.6	80	0.95	1.3	80	0.70	1.4
1000	100	1.45	0.7	100	1.12	1.5	110	0.68	1.9

^a The solution was 1.0 mM $\text{Ru}(\text{bpz})_3^{2+}(\text{PF}_6^-)_2$ and 0.1 M TBAFP in $\text{CH}_3\text{-CN}$ at 25⁰ C. $\Delta E_p = E_{pc} - E_{pa}$; C = concentration of complex. Peak currents for waves III and IV were measured from extrapolated decreasing current of preceding wave. The units for the current function evaluation were $i = \text{A}\cdot\text{cm}^{-2}$; $v^{1/2} = (\text{V}\cdot\text{sec}^{-1})^{1/2}$; C = M.



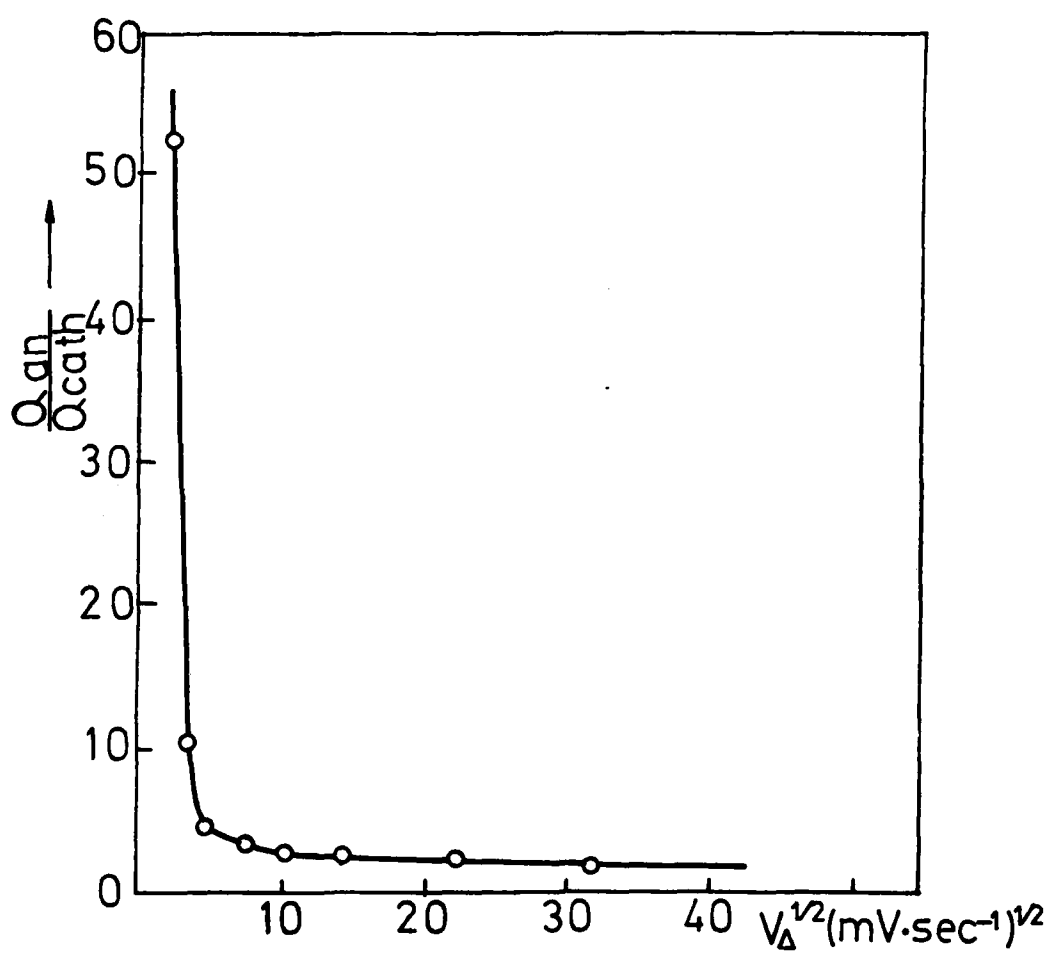


Figure 2

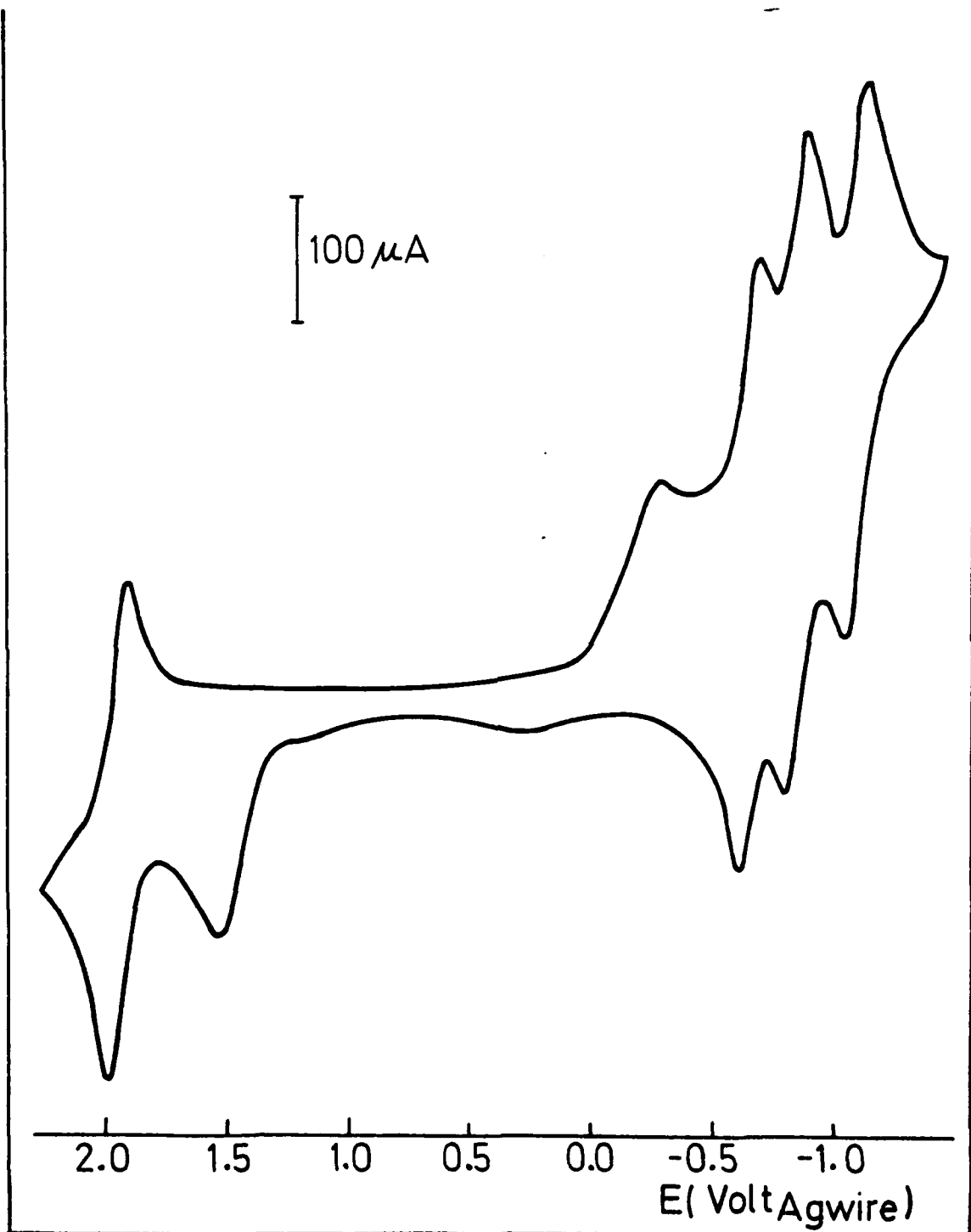


Figure 3

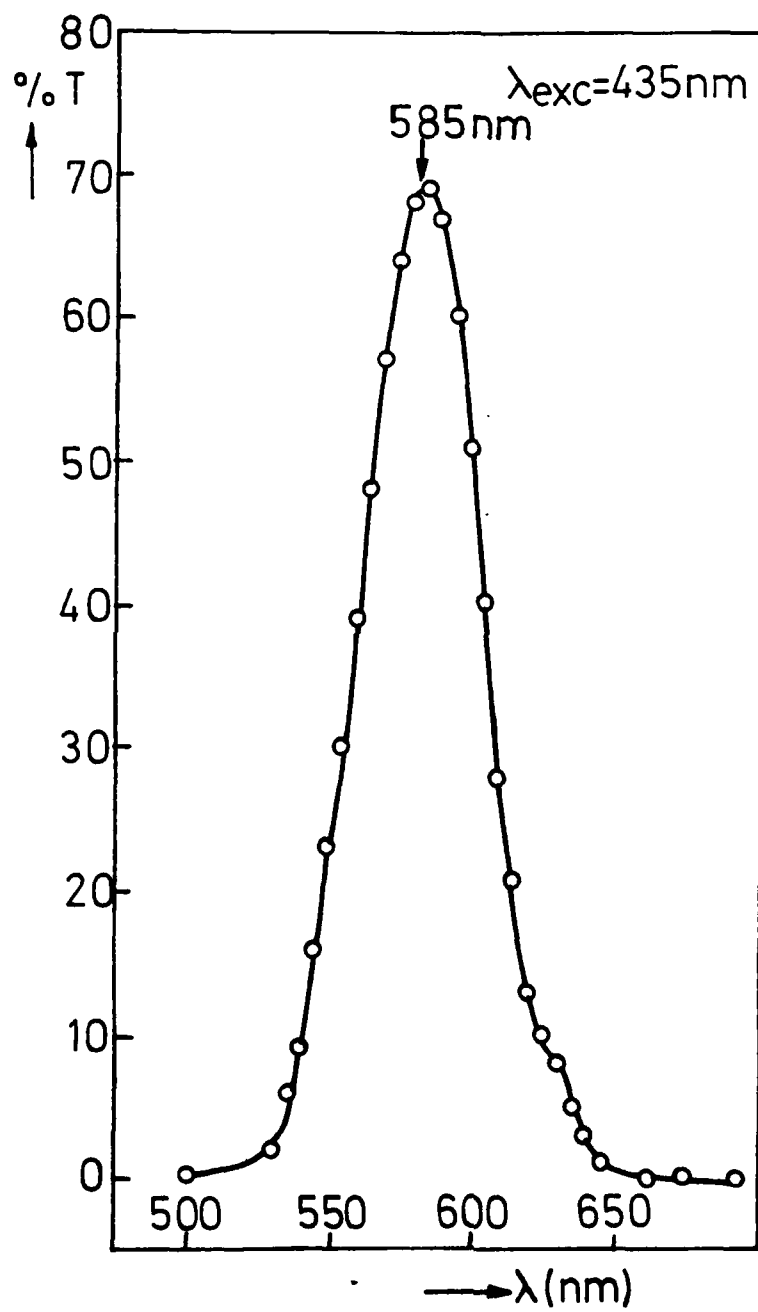


Figure 4

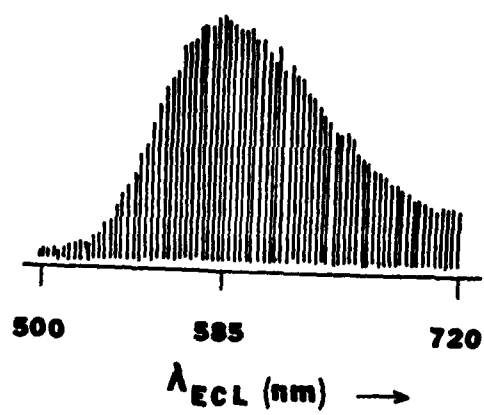
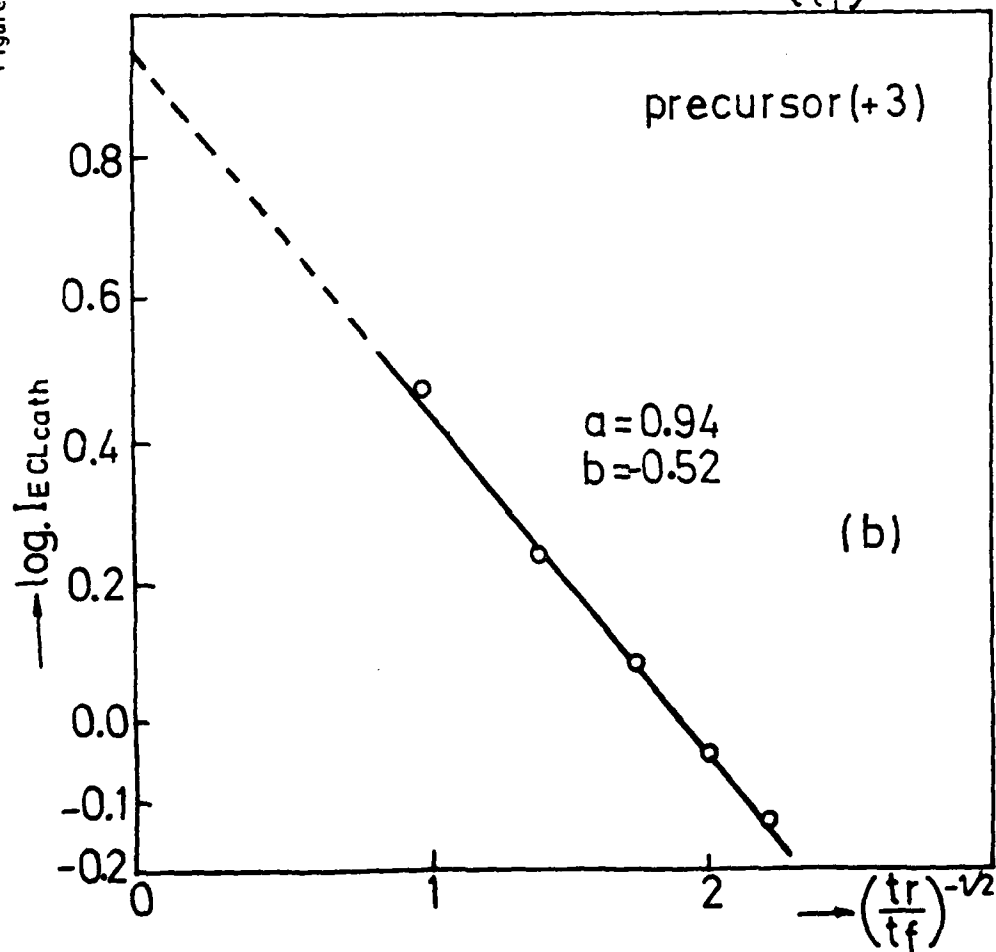
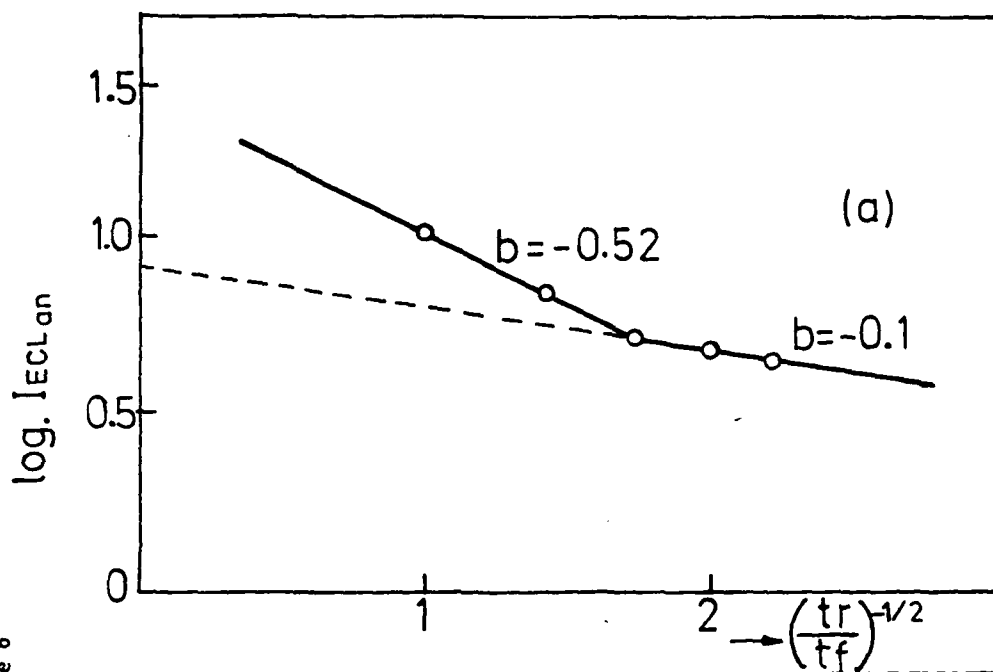


Figure 5

Figure 6



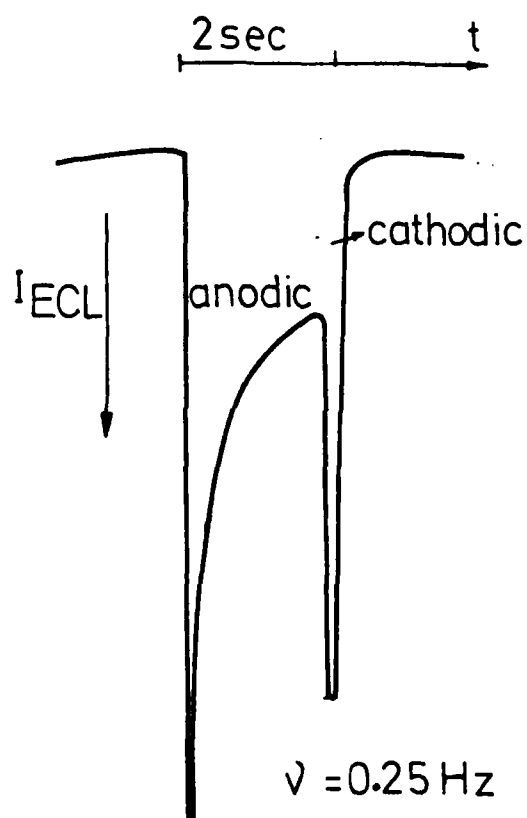


Figure 7

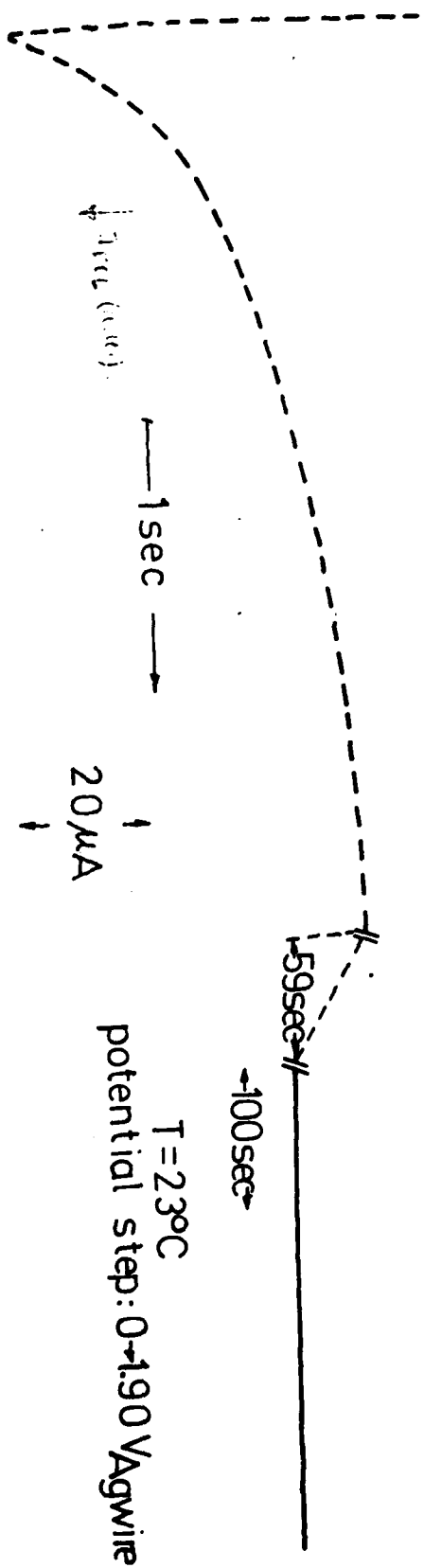


Figure 8

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